

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
9 October 2003 (09.10.2003)

PCT

(10) International Publication Number
WO 03/083974 A1(51) International Patent Classification⁷: H01M 6/14,
6/16, 6/18, 4/58, 4/60, 4/62

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(21) International Application Number: PCT/US03/08783

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(22) International Filing Date: 20 March 2003 (20.03.2003)

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(25) Filing Language: English

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,

(26) Publication Language: English

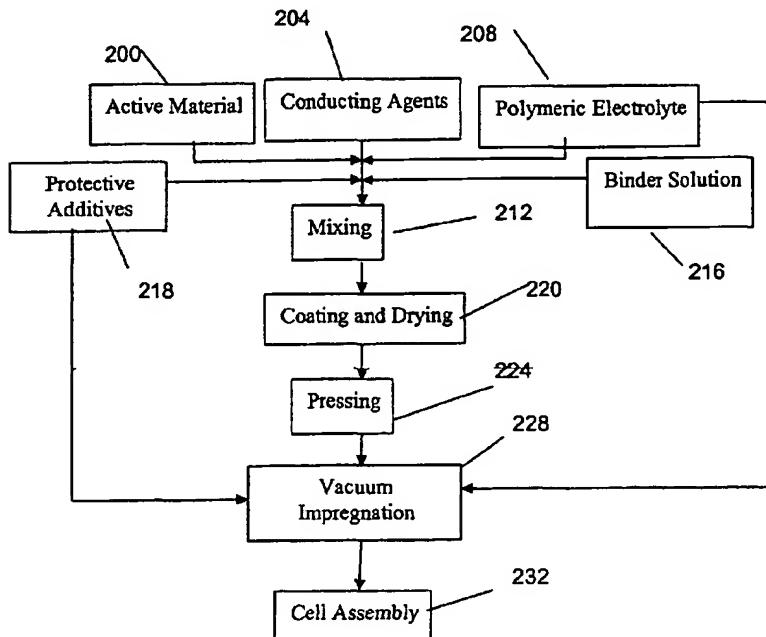
[Continued on next page]

(30) Priority Data:

10/104,352	22 March 2002 (22.03.2002)	US
10/167,940	12 June 2002 (12.06.2002)	US
PCT/US03/02128	22 January 2003 (22.01.2003)	US
PCT/US03/02127	22 January 2003 (22.01.2003)	US
60/443,892	30 January 2003 (30.01.2003)	US
60/446,848	11 February 2003 (11.02.2003)	US
60/451,065	26 February 2003 (26.02.2003)	US

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(54) Title: METHOD FOR FABRICATING COMPOSITE ELECTRODES



(57) Abstract: Disclosed is a method for manufacturing electrodes (100) for electrochemical devices such as batteries and capacitors in which a viscous polysiloxane polymer electrolyte (116) is incorporated into the slurry of materials forming the electrode (100). The optional addition of protective additives (218) to the slurry is also disclosed. A follow-on vacuum impregnation step (228) is disclosed to further improve penetration and wetting by the electrolyte (116).

WO 03/083974 A1



ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

METHOD FOR FABRICATING COMPOSITE ELECTRODES

REFERENCE TO PRIOR FILED APPLICATIONS

[0001] This application claims priority to copending provisional application serial number 60/451,065 entitled "Method for Fabricating Composite Electrodes" filed February 26, 2003; and to copending provisional application serial number 60/443,892 entitled "Nonaqueous Liquid Electrolyte" filed January 30, 2003; and to copending provisional application serial number 60/446,848 entitled "Polymer Electrolyte for Electrochemical Cell" filed February 11, 2002; and to PCT/US03/02127, filed January 22, 2003; and to PCT/US03/02128, filed January 22, 2003; and to copending US application serial number 10/167,490 filed June 12, 2002, which is a Continuation-in-Part of co-pending application Serial Number 10/104,352, filed March 22, 2002, the disclosure of each of which is incorporated herein in its entirety by reference, including all disclosures submitted therewith.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR
DEVELOPMENT

[0002] This invention was made with United States Government support under NIST ATP Award No. 70NANB043022 awarded by the National Institute of Standards and Technology (NIST). The United States Government has certain rights in this invention pursuant to NIST ATP Award No. 70NANB043022 and pursuant to Contract No. W-31-109-ENG-38 between the United States Government and the University of Chicago representing Argonne National Laboratory.

FIELD

[0003] The present invention relates to fabrication methods for polymer batteries using liquid polymer electrolytes. More particularly, the present invention relates to a method to improve the performance of liquid electrolyte alkali metal polymer batteries (especially,

lithium metal and lithium ion) including, rate, capacity, and cycle life. As used herein, "lithium battery" or "lithium ion battery" shall be defined as including batteries made with any alkali metals or alkaline earth metals whether or not a metal electrode is used.

BACKGROUND

[0004] The demand for the application of polymeric electrolytes has increased because of their impact on calendar life and safety of batteries. Conventional electrolytes with nonaqueous carbonate solvents and lithium hexafluorophosphate salts react violently with positive and negative electrodes in lithium ion batteries resulting in significant loss in calendar life and raising safety concerns. Therefore, the development of conductive liquid polymers that are nonvolatile and are resistive to oxidation and reduction could lead to new lithium ion polymer battery systems with long calendar life and improved safety performance. Electrolytes based on polymeric structures generally have better heat resistance than conventional carbonate based electrolytes. Although the electrolytes with polymeric structure have numerous advantages over the carbonate solvent based electrolytes, their application in lithium ion secondary batteries has been limited due to low ionic conductivity, usually below 10^{-4} S/cm at room temperature. Up to now, most liquid polymers such as siloxane or phosphorous hetero-polymers have very high viscosity and cannot be used in lithium ion batteries because of difficulty in effectively wetting the electrodes.

[0005] Polymer lithium batteries offer substantial advantages over lithium batteries with currently-known liquid electrolytes. Among these advantages are enhanced safety, long cycle life, high energy density, and flexibility. Polymer lithium batteries also hold great promise to be manufactured with ease, since thin film processes in the polymer industry can be used or adapted to the production of secondary lithium ion batteries.

[0006] One of the key issues in commercializing secondary lithium ion polymer batteries is the ionic conductivity of polymer electrolyte, which is essential for high rate operation of the lithium battery. Some polymeric electrolyte solutions can be applied to the electrolyte filling process in lithium ion secondary battery manufacture in the same way as the other electrolytes such as carbonate-based solutions. Lithium ion secondary batteries with the polymer as a conducting medium can be fabricated by injecting the polymeric electrolyte solution into a spiral jelly roll type cell or a stacked cell. It can also be coated onto the surface of electrodes and assembled with a porous separator to fabricate single or multi-stacked cells that are packaged within a plastic or plastic-coated aluminum type pouch. These techniques are well-known in the art; however, they are not suitable for viscous polymers such as siloxanes and phosphorous hetero-polymers because of their high viscosity.

[0007] In general, most liquid polymer electrolytes are more thermally stable and less volatile than low molecular weight chemicals such as carbonates. Therefore, the present inventors have investigated the wetting and penetration mechanism of viscous liquid polymer electrolytes and have developed a new electrode manufacturing process that incorporates the liquid polymer during the fabrication of the electrodes. The liquid polymer electrolytes used in the composite electrodes have beneficial characteristics such as high conductivity and stability at higher temperatures than are used for drying the solvent used to mix the binder.

[0008] The demand for a safer lithium battery for high power and high energy applications has led to substantial research and development activities in flame-retardant, solid polymer electrolyte and new concept electrolytes with improved thermostability. In addition, the increasing need for safe power sources for medical applications such as implanted batteries demands new approaches to manufacturing batteries that result in high reliability and safety without sacrificing capacity and rate capability.

[0009] To meet this demand, new nonvolatile, liquid polymeric electrolytes were developed. Electrolytes based on polymeric structure have fundamentally better heat resistance than conventional carbonate based electrolytes and can reduce many side chemical reactions occurring in lithium secondary battery under abnormal operating conditions such as temperatures exceeding 60°C. The present inventors have developed liquid polymer electrolytes that do not evaporate at temperatures up to 150°C, offer high ionic conductivity around room temperature, and have a wide electrochemical stability window. However, the high viscosity of these new polymer electrolytes inhibits effective penetration and wetting of electrode materials. Therefore, a need was seen to develop a new method to effectively manufacture batteries with viscous polymer electrolytes such as polysiloxane electrolytes.

BRIEF SUMMARY

[0010] The aim of this invention was to develop an engineering and manufacturing process that overcomes the problem of the viscous liquid polymers and permits the polymers not only to wet, but also to effectively penetrate the bulk of the electrode.

[0011] The present invention incorporates the polymer electrolyte mixed with the salt and conductive agent (e.g., acetylene black, natural graphite, artificial graphite, graphite whiskers, graphite fibers, metal whisker, metal fibers, etc.) in a slurry that contains the active material. The slurry may also contain a binder and/or a solvent (e.g., N-methylpyrrolidone (NMP), acetonitrile, or water) to adjust the casting viscosity. The slurry is then cast on or around the current collector and dried at temperatures around 120°C. This forms an electrode with much lower porosity than that in conventional lithium ion batteries. Preferably, the pore volume is equal to that of the volume of the solvent such as NMP used in dissolving the binder. Protective additives may also be incorporated. These additives form a passivation film (solid-electrolyte interface (SEI)), on the negative electrode and may suppress gas evolution.

Such additives may be incorporated into the electrolyte. Accordingly, the invention is a new fabrication method in which the electrode contains at least some of the polymer electrolyte when it is formed. These electrodes are highly suitable for electrochemical devices such as lithium batteries and capacitors. Additional penetration and wetting of the electrodes may be carried out after formation by the use of vacuum impregnation.

[0012] An object of the present invention is to provide a composite electrode structure, with improved capacity, cycling, and manufacturability.

[0013] A further object of the present invention is to provide a method of manufacture which is easily applied to the lithium ion electrode technology.

[0014] Yet a further object of the present invention is to provide an improved fabrication method for electrodes, especially for use in consumer products, electric and hybrid-electric vehicles, submarines, medical and satellite applications.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] Fig. 1 is a schematic of the composite electrode made according to the present invention.

[0016] Fig. 2 is a flow chart of the fabrication process for an electrode made according to the present invention.

[0017] Fig. 3 shows charge (Li de-intercalation) curves for three composite negative electrodes made according to the present invention.

[0018] Fig. 4 shows charge (Li de-intercalation) curves of composite electrodes made according to the present invention.

[0019] Fig. 5 is a cycling capacity graph for several composite electrodes made according to the present invention.

DETAILED DESCRIPTION

Table 1 summarizes experiments carried out with the purpose of cycling the electrode when using different methods of incorporating the polymer in the electrodes. As can be seen, all the processes of electrolyte filling (after casting of the electrode) were unsuccessful due to the high viscosity of the electrolyte and its inability to penetrate the electrode material.

Method	Description	Capacity (mAh/g)
Standard	Same as lithium ion coin cell	1.6
Vacuum treatment	Dip electrode into siloxane-PEO electrolyte and put it in vacuum for 20 min	91.8
Standard + High Temp. formation	Use standard method for cell assembly and 70°C, C/14 formation	5.0
Dilution with conventional liquid electrolyte & Standard	Dilute polysiloxane liquid* electrolyte with 1.2-M LiPF ₆ in EC:EMC(3:7) and use standard method to assemble cell	
	5% siloxane	143.0
	50% siloxane	102.0
	80% siloxane	35.6

*PMHS3B=3 oxygens, on side chain, no spacer:

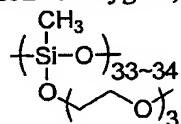


Table 1: Capacity of carbon materials and processes used for polymer electrolyte filling carbon-lithium metal cells.

[0020] To solve these major wetting and electrolyte penetration problems in the electrodes, a new manufacturing concept for the electrode fabrication is needed. The present inventors developed a process for mixing the polymer electrolyte directly with the active materials and binder during the process of slurry making. This process allows for an intimate

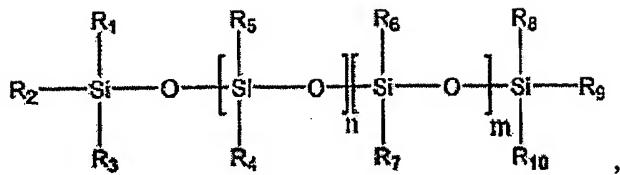
mix of the polymer with the active material providing lithium ion conductive network needed for cycling the electrodes. The liquid type polymeric electrolytes should be composed of nonvolatile compounds. In the case of lithium ion batteries, the amount of polymer during the mixing process should be equal to or greater than the volume of electrode. The electrode should contain about 20% to 60% pores.

[0021] Fig. 1 shows a schematic of composite electrode 100, which contains a positive or negative active material 102, conducting agent 104 (carbon black, graphite powder, and mixtures thereof), polymer binder (such as poly(vinylidene fluoride) (PVDF), styrene-butadiene rubber (SBR), acrylate binder, other rubber binders, and mixtures thereof) 108, current collector 112, and the liquid type polymeric electrolyte 116. The polymer electrolyte 116 is an integral part of the electrode. The density of composite electrode is preferably about 1.2 - 3.0 g/cc, but may be as high as about 8.0 g/cc.

[0022] The proposed composite electrode structure and its processing method yield high charge/discharge characteristics. A follow-on vacuum impregnation process after forming the composite electrode (containing polymer electrolyte) was effective in further improving the charge/discharge characteristics.

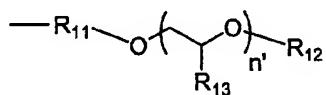
[0023] The polymeric electrolyte 116 is preferably a polysiloxane liquid. Its structure may take a variety of forms, including, but not limited to, any of the following, with or without propylene spacers between the Si atom of main chains and any PEO side chain.

General Formula I:



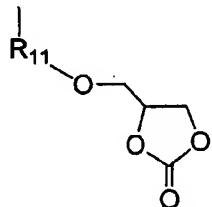
wherein, R₁, R₂, R₃, R₇, R₈, R₉ and R₁₀ are alkyl groups, preferably chosen from methyl, ethyl, propyl, and butyl; at least one of -R₄ and -R₅ is represented by General Formula II; R₆ is an alkyl group preferably chosen from methyl, ethyl, propyl and butyl or represented by General Formula III; n is equal to 3 to 200, m is equal to 0 to 200;

General Formula II:



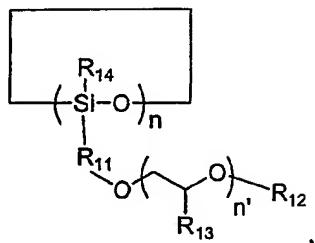
wherein, R₁₁ is nil or is an alkylene, preferably trimethylene, R₁₂ is alkyl group, preferably chosen from methyl, ethyl, propyl, and butyl, R₁₃ is hydrogen or an alkyl group, n' is less than about 20;

General Formula III:



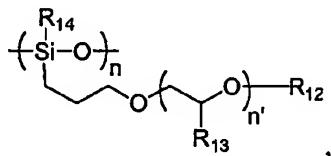
wherein, R₁₁ is nil or is an alkylene, preferably trimethylene.

General Formula IV:



wherein, R₁₁ is nil or is an alkylene, preferably trimethylene, R₁₂ is an alkyl group, preferably chosen from methyl, ethyl, propyl, and butyl, R₁₃ is hydrogen or an alkyl group, n is equal to 3 to 10, n' is less than about 20.

General Formula V:



wherein, R₁₂ and R₁₄ are alkyl groups, preferably chosen from methyl, ethyl, propyl, and butyl, R₁₃ is hydrogen or an alkyl group, n is equal to 3 to 200, n' is less than about 20.

[0024] General Formula V is considered the preferred structure. This molecule can be synthesized through hydrosilylation between polysiloxane containing Si-H bond and allyl terminated polyethylene glycol methyl ether.

[0025] Fig. 2 is a flow chart showing the steps of the fabrication process of composite electrodes and the cell. The process is similar to that traditionally used in lithium ion technology except for adding liquid polymer electrolyte to the slurry before the coating process and formation of electrodes. Therefore, this process is easy to implement for the mass production of electrodes. Specifically, active material 200, conducting agents 204 (e.g., graphite), and polymeric electrolyte 208 (e.g., poly(siloxane-g-ethylene oxide)) are mixed 212 with a binder solution 216 (e.g., PVDF, styrene butadiene rubber (SBR), acrylate binder,

acrylonitrile/butadiene rubber (NBR), isoprene, and natural rubber) and one or more protective additives 218. The resulting mixture is coated and dried 220 (onto a current collector and pressed 224. Next, the formed electrode is vacuum impregnated 228 with additional liquid polymer electrolyte 208 and, optionally, protective additives 218, to assure maximum penetration and wetting. Finally, the cells are assembled 232 into batteries according to conventional methods such as winding or stacking/laminating. Active materials may be any known material or combination of known materials such as LiCoO₂, LiNiO₂, LiNi_{1-x}Co_yMe₂O₂ (where Me is Mg, Ti, Zn, or Al), LiMn_{0.5}Ni_{0.5}O₂, LiMn_{0.3}Co_{0.3}Ni_{0.3}O₂, LiFePO₄, LiMn₂O₄, LiFeO₂, LiMn_{1.5}MeO₄ (where Me is Ni, Co, or Fe), or combinations thereof. The active material used is not limited as the present process is applicable to any such material now-known, insubstantially different from those now-known, or currently unforeseeable active materials which might be developed in the future.

[0026] Protective additives 218 may include any additives that decompose at voltages higher than 0.6 V and form a passivation film (SEI film) on the negative electrode. These include, but are not limited to, vinyl ethylene carbonate (VEC), vinylene carbonate (VC), ethylene carbonate (EC), and propylene carbonate (PC). Protective additives 218 may also include additives that suppress the gas evolution at the negative electrode, such as ethylene sulfide (ES) and ethylene ethyl phosphate (EEP). See, e.g., U.S. Patent 5,753,389 to Gan et al. (assigned to Wilson Greatbatch Ltd.); Aurbach et al., J. Electrochem. Soc., 143, 3809 (1996).

[0027] The additives are mixed with the liquid polymeric electrolyte and may be incorporated by the electrolyte vacuum impregnation process. Such protective additives will suppress the evolved gas generated by the decomposition of SEI film and will improve

cycling performance. Protective additives should preferably comprise no more than 50wt% of the total electrolyte.

[0028] The following example describes the manner and process of making a composite electrode and its cell according to the present invention.

[0029] A negative composite electrode mixture of 74% by weight of the graphite powder (GDR) and 18wt% of polysiloxane/LiTFSi binder electrolyte was prepared. In addition, 8wt% polyvinylidene fluoride (PVDF) was added as a binder to the composite mixture. The PVDF was dispersed into N-methylpyrrolidone to form a slurry or paste. The mixture of negative composite electrode was homogeneously mixed by ball milling for 12 hrs. The slurry was coated onto one face of a copper foil strip having a thickness of 20 μ m as a negative electrode current collector, was dried at 80°C in vacuum overnight, and was subjected to the roll press to form a strip negative electrode having a thickness of 65 μ m. A graphite electrode was punched out to form a negative electrode with 15 mm diameter, and then electrolyte was impregnated into the electrode in a vacuum over night.

[0030] Fig. 3 shows the effect of vacuum impregnation of siloxane polymer and electrode density on the charge/discharge characteristics. It may be seen that it is most effective to impregnate the electrodes with the liquid siloxane polymer electrolyte under a vacuum. Trace 300 represents the discharge cycle curve for a cell made with vacuum-impregnated electrodes with a density of 1.3 g/cc. This sample exhibited a capacity of about 300 mAh/g. Trace 304 shows the discharge cycle curve for a cell having vacuum-impregnated electrodes having 1.8 g/cc density. It had approximately 240 mAh/g capacity. Trace 308 is the discharge cycle for a cell with 1.8 g/cc density electrodes that were not vacuum-impregnated. This cell exhibited a capacity of only about 180 mAh/g, significantly less than either of the vacuum-impregnated cells tested. Electrodes were prepared by 74% GDR graphite powder,

8% PVDF binder with 18% 1-M LiTFSi/siloxane polymer electrolyte in NMP organic solvent. The mixture was coated onto copper foil, and dried under a vacuum. The electrodes were then tested in a 2016 coin cell. Lithium metal was used for the counter electrode with 1-M LiTFSi/siloxane polymer electrolyte. All the cells were tested at the C/20 rate.

[0031] In the present invention, a second solvent may be added as a protective additive to the liquid polymeric electrolyte, in order to improve the wettability of negative electrode, to form the SEI film on the graphite surface, and to suppress further decomposition of liquid siloxane polymer. Examples of preferred additives are EC, PC, and VEC. A coin-shaped test cell having a diameter of 20 mm and a thickness of 1.6 mm was prepared. The cell was made up of a counter electrode/Li metal; separator/porous film formed of polypropylene; electrolyte/solution obtained by dissolving LiTFSi in a liquid polysiloxane polymer; MCMB graphite composite electrode/ current collector/copper foil. A separator was used as a microporous polypropylene film having a thickness of 25 μ m.

[0032] Fig. 4 shows the capacity characteristics of Li metal/MCMB graphite composite electrode cell comprising polysiloxane liquid polymer/ lithium bis(oxalato) borate ("LiBoB") electrolyte containing 3% organic additive. The composition of MCMB composite was exactly same as that of above-mentioned GDR composite electrodes. Additional electrolyte was filled in by vacuum impregnation. Curve 320 shows the performance with no protective additives. Cells made with VEC, PC, and EC are shown by curves 324, 328 and 332 respectively. It may be seen that the addition of protective additives increased capacity versus the cell with no additives from just above 200 mAh/g to a range of 240 to 260 mAh/g, representing a minimum of 20% increase in capacity.

[0033] It is believed that capacity was increased by the supplementation of additional organic solvents because the organic additives worked as wetting agents to decrease the

viscosity of electrolyte and thus improve the wetting of the graphite electrode. Such additional solvents can also improve cycling performance at high rates.

[0034] Fig. 5 presents the cycling performance of the same type cells as in Figure 3. The cycling performance of the cell made with no additional protective solvents is shown by curve 360. The greatly improved performance by the addition of VEC, PC, and EC is shown by curves 364, 368, and 372, respectively. The cell with no additives 360 showed less than 150 mAh/g capacity after 10 cycles, while the cells with protective additive ranged from 200 to 240 mAh/g after 10 cycles.

[0035] It is believed that the organic additives of the present invention are reduced to form an SEI film which deposits on the graphite anode surface. This surface SEI film is electrochemically more stable and ionically more conductive than the SEI film formed in the absence of the organic additives. Thus, the surface SEI film so formed is believed responsible for improved cell performance.

[0036] The specific implementations disclosed above are by way of example and for the purpose of enabling persons skilled in the art to implement the invention only. We have made every effort to describe all the embodiments we have foreseen. There may be embodiments that are unforeseeable or which are insubstantially different. We have further made every effort to describe the invention, including the best mode of practicing it. Any omission of any variation of the invention disclosed is not intended to dedicate such variation to the public, and all unforeseen or insubstantial variations are intended to be covered by the claims appended hereto. Accordingly, the invention is not to be limited except by the appended claims and legal equivalents.

Claims

What is claimed is:

1. A method for making a composite electrode comprising the acts of:
 - a) mixing to form a slurry at least one of each of the following: active material, metal ion conducting liquid polymeric electrolyte, and conductive agent; and
 - b) casting said slurry in contact with at least one current collector.
2. The method recited in claim 1 wherein said metal ion is selected from the group consisting of: alkali metals and alkaline earth metals.
3. The method recited in claim 1 wherein said slurry further comprises at least one of the materials selected from the group consisting of: binder and solvent.
4. The method recited in claim 1 further including the act of drying said slurry.
5. The method recited in claim 1 wherein said alkali metal ion conducting liquid polymeric electrolyte comprises a siloxane polymer.
6. The method recited in claim 5 wherein the ratio of [EO]/[Li] in said polymeric electrolyte is about 5 to 50.
7. The method recited in claim 1 wherein said at least one active material is selected from the group consisting of: LiCoO_2 , LiNiO_2 , $\text{LiNi}_{1-x}\text{Co}_x\text{Me}_2\text{O}_2$ (Me: Mg, Ti, Zn, Al), $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$, $\text{LiMn}_{0.3}\text{Co}_{0.3}\text{Ni}_{0.3}\text{O}_2$, LiFePO_4 , LiMn_2O_4 , LiFeO_2 , and $\text{LiMn}_{1.5}\text{MeO}_4$ (Me: Ni, Co, Fe).
8. The method recited in claim 1 wherein said at least one active material comprises one or more negative active materials selected from the group consisting of: graphite, carbon, $\text{Li}_4\text{Ti}_5\text{O}_{12}$, tin alloys, and intermetallic compounds.
9. The method recited in claim 1 wherein said binder comprises at least one material selected from the group consisting of: PVDF, styrene-butadiene rubber (SBR), acrylate

binder, other rubber binders such as acrylonitrile/butadiene rubber (NBR), isoprene, and natural rubber.

10. The method recited in claim 9 wherein said binder comprises less than 50wt% of said composite electrode.
11. The method recited in claim 1 wherein said solvent comprises one or more materials selected from the group consisting of: N-methylpyrrolidone (NMP), dimethyl formamide, dimethyl acetamide, tetrahydrofuran, acetonitrile, and water.
12. The method recited in claim 1 wherein said conductive agent comprises one or more materials selected from the group consisting of: acetylene black, natural graphite, artificial graphite, graphite whiskers, graphite fibers, metal whiskers, and metal fibers.
13. The method recited in claim 1 wherein said mixing step further comprises mixing at least one protective additive.
14. The method recited in claim 13 wherein said at least one protective additive comprises one or more materials that decompose at voltages higher than 0.6 V and form a passivation film on the negative electrode.
15. The method recited in claim 14 wherein said at least one protective additive is selected from the group consisting of vinyl ethylene carbonate (VEC), vinylene carbonate (VC), ethylene carbonate (EC), propylene carbonate (PC), sulfur dioxide (SO₂), ethylene sulfide (ES), and ethylene ethyl phosphate (EEP).
16. The method recited in claim 13 wherein said protective additive comprises less than 50wt% of the total electrolyte.
17. A composite electrode made according to the method recited in claim 1.
18. The composite electrode recited in claim 17 wherein the density of said electrode is less than or equal to about 8.0 g/cc.

19. The composite electrode recited in claim 17 wherein the density of said electrode is less than or equal to about 3.0g/cc.
20. The composite electrode recited in claim 17 wherein the density of said electrode is about 1.2 to 3.0g/cc.
21. A composite electrode made according to the method recited in claim 5.
22. The composite electrode recited in claim 21 wherein said alkali metal is lithium.
23. An electrochemical device comprising at least one electrode made according to the method recited in claim 1.
24. A method for making an electrochemical device comprising the acts of:
 - a) providing a positive composite electrode made according to the method recited in claim 1;
 - b) providing a porous separator;
 - c) providing a negative composite electrode made according to the method recited in claim 1;
 - d) placing said porous separator between said positive electrode and said negative electrode;
 - e) placing the combination of said positive electrode, said porous separator, and said negative electrode in a container;
 - f) vacuum impregnating said electrodes with metal ion conducting liquid polymeric electrolyte; and
 - g) sealing said container.
25. The method recited in claim 24 wherein said metal ion is selected from the group consisting of: alkali metals and alkaline earth metals.
26. The method recited in claim 24 wherein said positive composite electrode further comprises at least one protective additive.

27. The method recited in claim 24 wherein said impregnating act further comprises vacuum impregnating said electrodes with a protective additive.
28. The method recited in claim 24 further comprising the act of rolling said combination of said positive electrode, said porous separator, and said negative electrode into a spiral roll.
29. The method recited in claim 24 further comprising the acts of stacking said combination of said positive electrode, said porous separator, and said negative electrode.
30. The method recited in claim 24 further comprising the act of combining said porous separator, said negative electrode, and more than one said positive electrode into a stack of alternating positive and negative electrodes separated by said porous separator.
31. An electrochemical storage device made according to the method recited in claim 24.

1/5

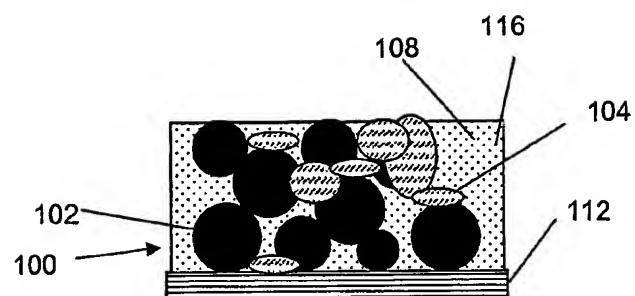


Fig. 1

2/5

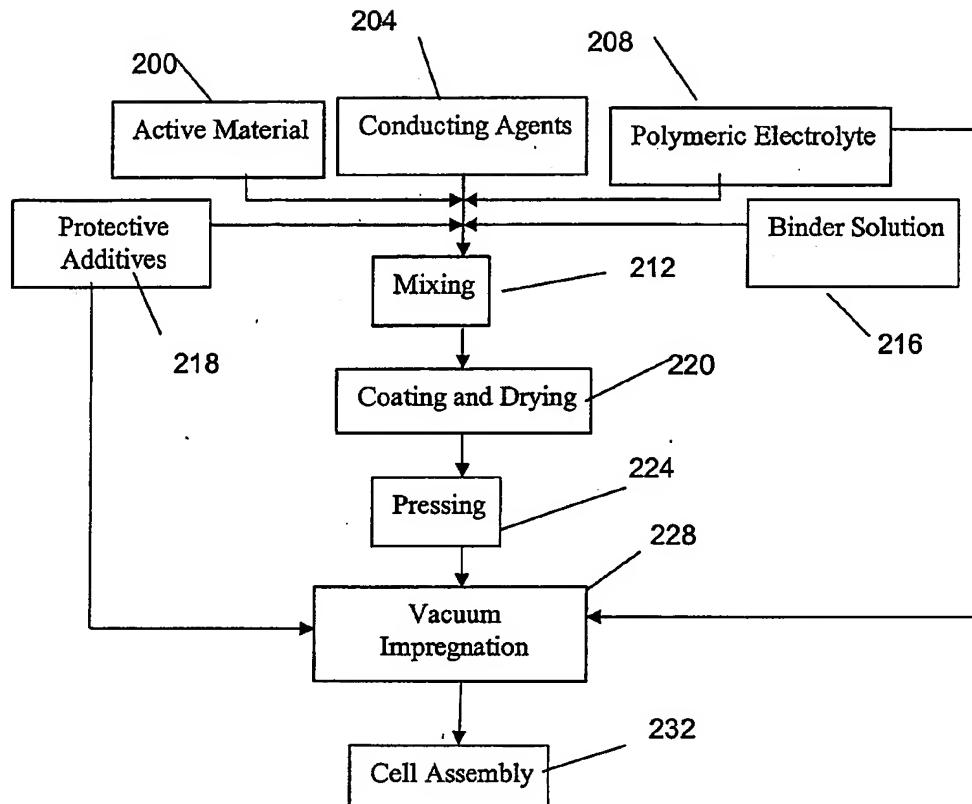


Fig. 2

3/5

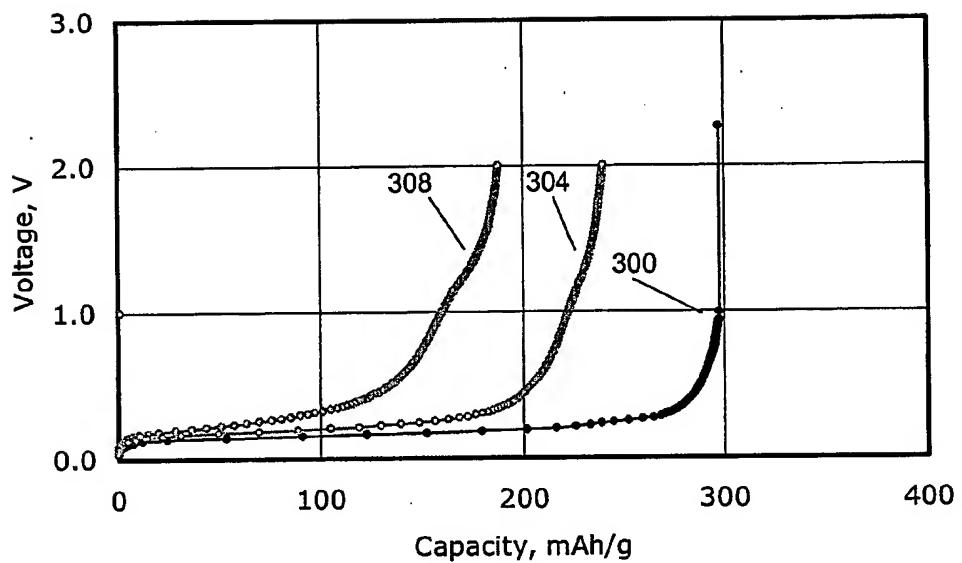


Fig. 3

4/5

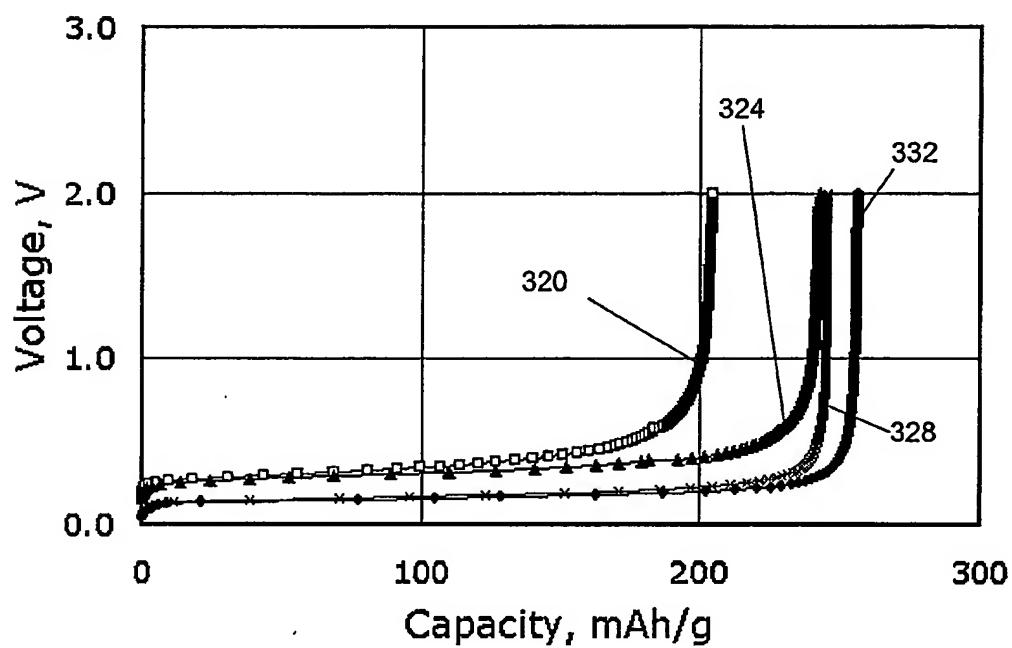


Fig. 4

5/5

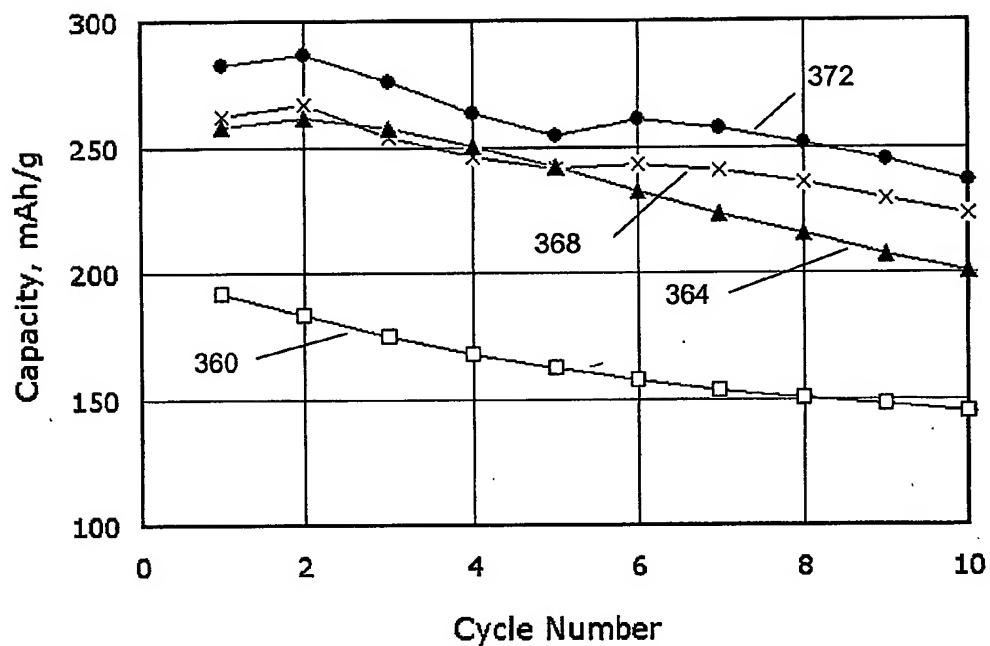


Fig. 5

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US03/08783

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : H01M 6/14, 6/16, 6/18, 4/58, 4/60, 4/62
 US CL : 29/632.1; 429/188, 189, 212, 217, 231.1, 231.8, 232, 302-304, 309, 313, 322
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 U.S. : 29/632.1; 429/188, 189, 212, 217, 231.1, 231.8, 232, 302-304, 309, 313, 322

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,419,984 A (CHALONER-GILL et al) 30 May 1995 (30.05.1995), col. 6, line 35-col. 7, line 10 and Examples 1-2.	1-5,7-10,12-17,21-23
Y		6,11,18-20,24-31
X	US 5,362,493 A (SKOTHEIM et al) 08 November 1994 (08.11.1994), col. 4, lines 7-17, claims 1-2.	1-5,8,12,17,21-23
Y		6,7,9-11,13-16,18-20,24-31
Y	US 5,112,512 A (NAKAMURA) 12 May 1992 (12.05.1992), col. 3, lines 23-47 and col. 5, lines 35-43.	1-31
Y	US 5,538,812 A (LEE et al) 23 July 1996 (23.07.1996).	1-31
Y	US 6,124,062 A (HORIE et al) 26 September 2000 (26.09.2000), col. 4, line 39-col. 6, line 61.	1-31
A	US 5,885,733 A (OHSAWA et al) 23 March 1999 (23.03.1999).	1-31

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier application or patent published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

14 July 2003 (14.07.2003)

Date of mailing of the international search report

04 AUG 2003

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